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(54) Curable polybutadiene modified epoxy resin

(57) Curable epoxy resin is produced by reacting a carboxyl terminated polybutadiene or carboxyl terminated butadiene-styrene copolymer with bisphenol-epichlorohydrin epoxy resin or hydrogenated bisphenol-epichlorohydrin epoxy resin, the components being present in a ratio of 1.8 to 30 equivalent of the epoxy resin component per 1.0 equivalent of the carboxyl component. The reaction is carried out at 80°C to 250°C for 1 to 20 hours.

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## SPECIFICATION

## Curable epoxy resin

5 The present invention relates to a method of producing a curable epoxy resin and to a resin produced by such method, the resin being suitable for production of paint, an impregnating material, a moulding material or laminated material. 5

Hitherto, epoxy resin, unsaturated polyester, silicone resin and polybutadiene resin have been used in the manufacture of such products. However, unsaturated polyester resin causes a high exothermal phenomenon and has a high shrinkage rate during curing. Further, it has inferior resistance in cyclic "cold-hot" changes and in consequence of its material inclusions, it can cause cracking and has inferior adhesiveness. In addition, it has high rates of dielectric constant and dielectric tangent and inferior thermal resistance. Silicone resin has superior electric properties, but inferior mechanical strength. In addition, it is expensive and is deficient in adhesiveness. Polybutadiene resin has superior electric properties and high chemical resistance, but it causes a high exothermal phenomenon and has a high shrinkage rate during curing. Further, it has inferior impact strength and poor resistance to cracking. Epoxy resin possesses surpassing mechanical properties and superior adhesiveness, but on the other hand, it has a poor resistance to delamination, inferior flexibility and insufficient impact strength. 10 15

20 In order to overcome the drawbacks of epoxy resin, polyethylene glycol, coal tar, dibutyl-phtahlate, polyglycol-glycidyl ether, glycidyl ester of organic fatty acid, polyester, polyamide, polyether and polythiol and the like have been used as a flexibility modifier in the resin combination. Further, the epoxy resin has been used admixed with an epoxy resin modified with urethane or an acrylonitrile-butadiene copolymer, but generally this method results in a cured material with less satisfactory electrical and mechanical properties. 25

In Japanese patent specification No. 10637/1978 there is disclosed a process in which a polybutadiene-polycarboxylic acid is reacted with an epoxy resin containing two  $(\alpha)(\beta)$ -epoxy groups having a methyl group at its  $(\beta)$ -position, the produced epoxy resin being modified with polybutadiene. In Japanese patent specification No. 144958/1978 there is disclosed a process which comprises reacting a polybutadiene having a terminal carboxyl group with an epoxy resin, and using the produced epoxy resin modified with polybutadiene. 30

According to the process disclosed in Japanese patent specification No. 10637/1978, the employable epoxy resin is defined as  $(\alpha)(\beta)$ -epoxy resin having a methyl group at its  $(\beta)$ -position. In the event of using an epoxy resin other than the specified resin, a gelling phenomenon arises in the reaction system in the course of a modification reaction of polybutadiene polycarboxylic acid and the epoxy resin, and consequently the desired epoxy resin modified with polybutadiene cannot be obtained. 35

According to the process disclosed in Japanese patent specification No. 144958/1978, a modified resin used in a step of obtaining an epoxy compound modified with polybutadiene has an inferior compatible solubility and its reaction compound is separated into two phases prior to a curing step or in the course of a heating and curing step. There is no suggestion of any means of avoiding an unhomogeneous cured material or of a procedure for inhibiting the gelling phenomenon in a reaction system at an esterification reaction step. In practice, according to above-mentioned known processes the reaction system for producing the modified epoxy resin causes a gelling phenomenon in the course of its modification reaction step and as a result a modified epoxy resin with good stability cannot be obtained. 40 45

According to a first aspect of the present invention there is provided a method of producing a curable epoxy resin, comprising the step of reacting a carboxyl terminated polybutadiene or a carboxyl terminated butadiene-styrene copolymer with an epoxy resin selected from the group consisting of bisphenol-epichlorohydrin type epoxy resin and hydrogenated bisphenol-epichlorohydrin type epoxy resin in the ratio of 1.8 to 30 equivalent of the epoxy resin component per 1.0 equivalent of the carboxyl component at a temperature of 80 to 250°C for 1 to 20 hours. 50

According to a second aspect of the present invention there is provided a curable epoxy resin when made by a method according to the first aspect of the invention.

55 A curable epoxy resin produced in accordance with a method exemplifying the present invention provides a homogeneous transparent cured material which possesses good mechanical properties, favourable adhesion, improved flexibility, impact strength, resistance to cyclic hot-cold changes and resistance to cracking.

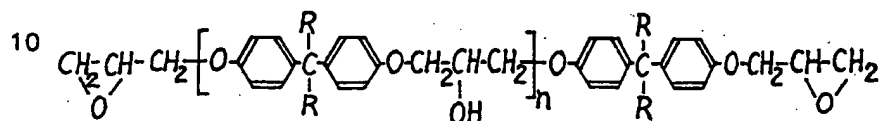
The carboxyl terminated polybutadiene or the carboxyl terminated butadiene-styrene copolymer for the curable epoxy resin is sold in the market under the following trade names: Nisso-PB-C-1000 and C-2000 (Nippon Soda Co. Ltd.), Hycar-CTB and CTBX (Goodrich Co. Ltd.), Telogen CT, S (General Tire Co. Ltd.) and Butarez CTL (Phillips Co. Ltd.). 60

In addition, a resin obtained by a process which comprises reacting a polybutadiene homopolymer or copolymer having a hydroxy terminal group (for example, Nisso PB-G-1000, 2000 & 3000 as trade names for products of Nippon Soda Co. Ltd., Poly-BD as trade name for 65

a product of ARCO Co. Ltd., Butarez HT as trade name for a product of Phillips Co. Ltd., Hycar-HTB as product of Goodrich Co. Ltd. and Telogen HT as trade name for a product of General Tire Co. Ltd.), with an acid anhydride, such as maleic anhydride and succinic anhydride, by means of a conventional semi-esterifying reaction step, can be used as the polybutadiene

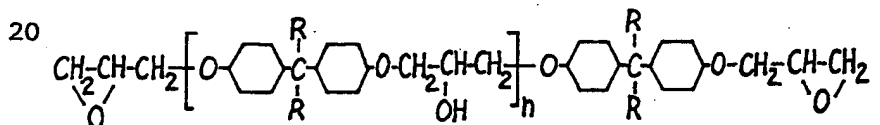
5 homopolymer or copolymer having the terminal carboxyl group.

The epoxy resin employable as a component of the reaction may be selected from the group consisting of bisphynol-epichlorohydrin-type epoxy resin having the formula:



15 (wherein  $n = 0$  to 20 and  $R = \text{H}$  or  $\text{CH}_3$ )

and hydrogenated bisphenol-epichlorohydrin-type epoxy resin having a formula:



25 (wherein  $n = 0$  to 20 and  $R = \text{H}$  or  $\text{CH}_3$ )

The bisphynol-epichlorohydrin-type epoxy resin is sold in the market under the following trade names: Epikote-827, 828, 834, 1001, 1004 and 1007 (Shell Chemical Co. Ltd.), Araldite-CY-250, 252, 260, 280, 6071, 6084 and 6097 (Ciba-Geigy Aktien Gesellschaft), DER-330, 331, 30 337, 661 and 664 (Dow Chemical Co. Ltd.) and Epichlon-800, 1000, 1010 and 3010 (Dai-Nippon Ink & Chemicals, Inc.).

The hydrogenated bisphenol-epichlorohydrin-type epoxy resin is sold in market under the trade name Adeka Resin EP-4080 (Asahi Electro-Chemical Ind. Co. Ltd.).

The reaction of the said carboxyl terminated polybutadiene or carboxyl terminated butadiene-styrene copolymer with the said epoxy resin is carried out at the rate of 1.8 to 30 mol equivalent, preferably 2.0 to 20 mol equivalent, of the epoxy group of per 1.0 mol equivalent of the carboxyl group at a reaction temperature of  $80^\circ\text{C}$  to  $250^\circ\text{C}$ , preferably at a temperature of  $100^\circ\text{C}$  to  $190^\circ\text{C}$ , until the acid value of the reaction product may be less 1.0. Usually, its reaction time is chosen from a range of 1 to 20 hours, preferably from a range of 2 to 10 35 40 hours.

This reaction mainly comprises a reaction of the epoxy group with the carboxyl group and a formation of the ester bond. A residue of the ester bond simultaneously produces a hydroxyl group.

If the molar number of the epoxy group is chosen to be less than 1.8 equivalent per 1.0 mol equivalent of the carboxyl group, there results from the reaction a higher molecular compound with an increased viscosity, so that in some instances a gelling phenomenon may occur. Such a rate is therefore not desirable. 45

On the other hand, if the mole number of the epoxy group is chosen to be more than 30 equivalents per 1.0 mol equivalent of the carboxyl group, an increased residual amount of non-reacted epoxy resin results and thereby the delamination strength, flexibility and impact strength 50 of the cured material are reduced.

In order to accelerate the reaction of the epoxy group with the carboxyl group, but to prevent an undesirable increase in viscosity or occurrence of a gelling phenomenon with consequent effect of thermal polymerization of the polybutadiene, by means of abbreviating the reaction time at high temperature, an accelerator can be added to the reaction system and thereby the 55 reaction can be accelerated.

An accelerator employable for above-mentioned purpose comprises, for example, 2-ethyl imidazole, tetraethyl-ammonium bromide, benzyldimethylamine, triethylenediamine, triethylamine, diethylamine, butylamine, benzyldimethylamine, choline chloride, caustic potash and alkali 60 carbonate. The accelerator can be added in an amount in a range of 0.01 to 5.0 molar percent in proportion to the epoxy group.

Further, in order to prevent the aforementioned thermal polymerization, a radical polymerization inhibitor can be added in an amount of 100 to 1,000 ppm to the reaction, the inhibitor comprising, for example, hydroquinone, para-benzoquinone or anthraquinone.

65 An inert gas may be used as the atmosphere for the reaction or else the reaction can be

65

carried out in the presence of air and thereby thermal polymerization for a part of the double bond of carbon-carbon can be more securely prevented. Furthermore, if necessary, an appropriate solvent may be used and in that event handling of the reaction compound is facilitated.

- 5 An epoxy resin modified with polybutadiene and obtained by a method exemplifying the present invention contains at least a non-reacted epoxy group and a hydroxyl group, so that it has a thermally curable nature. By means of blending an appropriate amount of a conventional epoxide curing agent, its curing and crosslinking reaction can take place readily at a temperature ranging from room temperature to a relatively high temperature and the resulting cured material
- 10 has superior properties and improved flexibility and impact resistance.

For the epoxide curing agent there can be used an amine or amines such as diethylene-triamine and a meta-phenylene-diamine, a carboxylic acid anhydride such as dodecenoic anhydride and maleic anhydride, a complex compound of boron trifluoride ( $\text{BF}_3$ ), such as mono ethylamine-boron trifluoride ( $\text{BF}_3$ ) and pyridine-boron trifluoride ( $\text{BF}_3$ ), a complex compound of

15 triethanolamine-borate, titanium alkoxide or a compound having one or more of -SH group, -NCO group, -NCS group, and -CONH group in its molecule. The amount of the epoxide curing agent that is used is chosen so that the ratio of an equivalent of the functional group proportional to an equivalent of the epoxy group is in the range of 0.8 to 1.2 in the epoxy resin modified with polybutadiene.

- 20 In order to reduce the viscosity of the epoxy resin modified with polybutadiene, a reactive diluent for conventional epoxy resin, such as butylglycidyl-ether, phenylglycidyl-ether and vinylcyclohexene-diepoxy, may be admixed therewith.

In using a resin obtained by a method exemplifying the present invention as an electric insulating casting material, an impregnating material, a thicker coating material or a moulding

25 material, the resin can be mixed with a reactive diluent and a filler, if necessary, together with a flame retarder, a reinforcing agent, a pigment, a plasticizer and an antioxidant or the like. The resin and these additives are fully intermixed so as to provide a resin composition which can be cured by heating or at room temperature. The curing process can be carried out in any one of the following ways: (1) adding the epoxide curing agent as a crosslinking agent, reacting it with

30 the epoxy group and thereby carrying out its crosslinking reaction; (2) adding a radical polymerization initiator as a crosslinking agent and thereby causing an unsaturated double bond of butadiene chain to participate in the crosslinking reaction; and (3) adding both components of the epoxide curing agent and the radical polymerization initiator and thereby carrying out the crosslinking reaction with both of the epoxy group and the unsaturated double bond.

- 35 A preferred one of the three curing processes can be determined by taking in consideration the electrical and mechanical properties, flexibility and thermal resistance required for the final product.

As the radical polymerization initiator there can be used individually or as mixtures a diacylperoxide such as benzoyl peroxide, 2,4-dichloro-benzoyl-peroxide, octanoyl peroxide and

40 lauryl peroxide; a dialkyl peroxide such as di-tertiarybutyl-peroxide and di-cumyl-peroxide; a perhydrox-ester such as tertiary-butyl-perbenzoate, tertiary-butyl-peracetate, di-tertiary-butyl-perphthalate and 2,5-dimethyl-2,5-di(benzoyl-perhydroxy)hexane; a ketone peroxide such as methyl-ethyl-ketone-peroxide and cyclohexanone peroxide; and a hydroperoxide such as tertiary-butyl-hydroperoxide, cumene-hydroperoxide,  $\alpha$ -phenyl-ethyl-hydroperoxide and cyclohexenyl-hydroper-

45 oxide. A non-foaming radical polymerization initiator is preferably used and preferably in an amount of 0.1 to 10 percent by weight, preferably 0.5 to 5.0 percent by weight in proportion to the total resin component.

As a curing accelerator, there can be used, for example, an amine compound such as dimethylaniline and diethylaniline and a metal salt such as a cobalt linolenate, lead octenate,

50 cobalt octenate, zinc naphthenate and manganese salt of rosin acid. The amount of the amine compound used is preferably from 0.1 to 5 percent by weight in proportion to the total resin component and the amount of carboxylic acid used is preferably 0.001 to 1.0 percent by weight as a metal component in proportion to the total resin component.

As the filler there can be used a precipitating material or inorganic material such as calcium

55 bi-carbonate, silica, talc, alumina, aluminium hydroxide, diatomaceous earth, clay, kaolin, mica, sand, glass powder, glass beads and barium sulfate, or a metal powder such as iron powder, aluminium powder, copper powder or a mixture thereof. The amount used is preferably 50 to 300 percent by weight in proportion to the total resin component.

As the reinforcing material, there can be used a fibrous material such as glass fibre, nylon

60 fibre, polyester fibre, polyvinylformal fibre, asbestos fibre, iron fibre, aluminium fibre or copper fibre. The amount used is preferably 2 to 100 weight percent in proportion to the total resin component.

As the plasticizer, there can be used a conventional plasticizer such as dibutylphthalate, dioctylphthalate, tricresyl phosphate and chlorinated paraffin, a tar such as petroleum tar and

65 coal tar, a petroleum oil such as naphthene base oil and paraffin base oil (including its

processed oil), an oil or a fat such as linseed oil, body-linseed oil, soyabean oil, body-soyabean oil, tung oil, safflower oil and castor oil, a resin such as polystyrene and tall resin, and a petroleum resin such as aromatic hydrocarbon resin and aliphatic cyclic hydrocarbon resin (for example, Mitsui Petrosin and Mitsui Hairetz, products of Mitsui Chemical Industry Co. Ltd.). An agent which is sufficiently flexible to be capable of feeding and which normally is fluid is particularly effective for improving the fluid nature of an insulating composition made from resin exemplifying the invention.

As the reactive diluent, a diluent for the polybutadiene resin may be used in addition to the diluent of the epoxy group. As this reactive diluent, vinyl monomer is preferred, the vinyl monomer comprising, for example, styrene, methyl styrene, vinyl toluene, methyl methacrylate, divinylbenzene, ethylfumarate or diallylphthalate. Styrene and vinyl toluene are preferred, and preferably are used in an amount of 10 to 90 percent by weight in proportion to the total resin component.

Further, there may be used a plasticiser for the purpose of reducing the initial viscosity of the resin, facilitating the mixture of the fillers and improving the feedability and elasticity of a moulding product made from resin exemplifying the invention. The plasticizer may be a phthalate ester such as dibutyl phthalate and dioctyl phthalate; a phosphate ester such as tricresyl phosphate and diphenyloctyl phosphate; a dibasic acid ester such as dibutyl sebacate, dioctyl sebacate and di-2-ethylhexyl-adipate; or a mixture of these substances. The plasticizer is used in an amount of 0.1 to 100, preferably 1.0 to 10.0, percent by weight in proportion to the total resin component.

The anti-oxidant employable for improving thermal resistance in a process exemplifying the present invention may be, for example, an alkyl phenol such as 4,4'-thiobis-(6-tertiary-butyl-3-methylphenol), 3,5-di-tertiary-butyl-3-hydroxy-toluene, 2,2'-methylene-bis-(4-methyl-6-tertiary butyl phenol) and 4,4'-butylidene-bis-(6-tertiarybutyl-3-cresol); an arylamine such as phenyl-G-naphthyl amine and N,N'-di- $\beta$ -naphthyl-p-phenylenediamine; a thionate ester of fatty acid such as dilauryl-thiodipropionate, distearyl-thiodipropionate and lauryl-steryl-thiodipropionate; or a mixture of these substances.

The selected anti-oxidant is preferably one which does not consume the active oxygen of the organic peroxide. It is preferably used in an amount of 0.01 to 10, preferably 0.1 to 2.0, percent by weight in proportion to the total resin component.

If it is necessary to impart a high degree of combustion resistance to an insulating resin composition exemplifying the present invention, a conventional flame retardant can be added thereto. As the inorganic flame retardant there can be used, for example, aluminium hydroxide (i.e. hydrated alumina), zinc borate or an organic halide such as chlorinated paraffin, benzene tetrachloride, benzene hexachloride, diphenyl chloride, triphenyl chloride, polyphenyl chloride a polymer of 3,3,3-trichloropropane oxide, perchloro-pentacyclodecan, "Dechloranplus" or "Dechloran" (the two last-mentioned being the trade names of products of Hooker Chemical Co., Ltd.).

As a bromide flame retardant there can be used, for example, tetrabromoethane, tetrabromobutane, tetrabromoacetylene, hexabromobenzene, tribromotoluene or hexabromododecan; an aryl ester such as tribromophenol, dibromopropyl ether of tribromo-phenol, bis-aryl-ether of tetrabromo-bisphenol A, bis-dibromopropyl ether of tetrabromo-bis-phenol A, pentabromodiphenyl ether, octabromobiphenol, HB (trade name of a product of Teijin Chemical Industry Co., Ltd.) or Pyrocard SR-100 (trade name for a product of Dai-ichi Industrial Pharmaceutical Co., Ltd.).

As a chlorobromide flame retardant there can be used, for example, dichlorotetrabromoethane or dibromotetrachloro-ethane-and-2-chloro-1,2,3,4-tetrabromo-ethane.

As a phosphate flame retardant containing a halogen component there can be used, for example, tris ( $\beta$ -chloroethyl) phosphate, tris (chloropropyl) phosphate, tri (dichloropropyl) phosphate, tris (2-bromoethyl) phosphate, tris (2,3-dibromopropyl) phosphate, tris (dibromobutyl) phosphate, tris (bromochloropropyl) phosphate, tris (2-chloroethyl) phosphate, tris (2-bromo-2-chloroisopropyl) phosphate and tris (1-bromo-3-chloroisopropyl) phosphate.

In addition, tribromophenol-acrylate, pentabromophenolmethacrylate, pentabromophenolacrylate, trichlorophenol-methacrylate, trichlorophenol-acrylate, pentachlorophenol-methacrylate and pentachlorophenol-acrylate are usable as the flame retardant.

As a promotor for the flame retardant there can be used, for example, antimony trioxide, phosphorus, a phosphorus compound, an organic peroxide, a metal oxide such as zinc oxide or stannic oxide and an organic amine. If the promotor is used in combination with a halide compound, a synergistic effect will occur.

In use of a polybutadiene modified epoxy resin product exemplifying the present invention, an appropriate amount of polybutadiene homopolymer or copolymer, acrylic modified polybutadiene and/or its hydrogenated polybutadiene or an epoxy compound may be added to the product to provide various properties which are required for an electric insulating material.

A curable epoxy resin which contains, as a main component, a polybutadiene modified epoxy

resin obtained by a process exemplifying the present invention may have superior mechanical properties, improved flexibility and excellent electric properties. Accordingly, it is suitable as a raw material for producing an electric insulating material, a moulding material, a paint composition, an adhesive agent and a construction material, and further it is useful as a civil engineering material.

Practical examples of use of the resin composition are electric insulating materials or paint materials such as varnish impregnated in a coil, varnish for coating cloth tubes, varnish for coating electric wires, paint for finishing solid surfaces and core varnishes.

The resin composition can also be used as a casting material in the manufacture of condensers, flyback transformers, cable connecting materials, resistors, transistors, electric motors, transformers, dynamos, insulators, bushings and analogous parts.

The resin composition can also be used as a moulding material for moulding electric parts such as connectors, switch gear, condensers, transistors, resistors, insulators, bushings, breakers, sockets, plug sockets, and switchcases; parts of chemical apparatus such as valves, cocks, pipejoints, impellers and bumps; and parts of automobiles, bicycles, ships and boats, such as casings, distributors, caps, brakes and clutches. Further, the composition can be used as a mechanical constructional material for pallets, containers, dinner ware, tiles, artificial marble and artificial garden decoration stones, or as a laminating material for electrical components such as FRP pipes, base plates for printed circuits, plates for electric ranges, radar domes and microwave parts.

Further uses of the resin are as materials for chemical apparatus such as FRP pipes for setting pipings and reaction tanks, and mechanical constructional materials for rocket engines, parts of ships and boats, FRP corrugated plates, bath tubs and lids of electrolytic tanks.

A paint material incorporating the resin can be an aqueous paint, a non-solvent type of paint or a powder paint. Such paints can be made in the form of thicker laminar coating paints, anticorrosive paints and non-tar epoxy paints, for coating bridge legs, metal cans, harbour facilities, ships, water treating facilities and iron reinforcing bars of pre-fabricating houses.

An adhesive incorporating the resin can be used with metals, textiles, rubber, wood, plastic films and resins. A civil engineering material incorporating the resin can be used as an asphalt road paving material, a non-slip road paving material, a water sealing material for tunnels, a sealant, a material for paving aircraft runways, a jointing material for mortar, and analogous materials. A construction material including the resin can be used as an asphalt waterproofing material, a road-crack injection material, a sealant and a walling material.

Methods exemplifying the present invention will now be more particularly described with reference to the following examples, in which unless otherwise specified, "part" means "part by weight".

#### Example 1

100 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1,560 and acid value: 60) were reacted with 100 parts of bisphenol-A diglycidyl ether (epoxy equivalent: 190) at 145°C for 3.5 hours by blowing nitrogen gas in a reaction system. A light yellowish transparent resin (Resin I) having an acid value of 0.1 or less was obtained.

Then, 100 parts of the Resin I were mixed with 30 parts of hexahydrophthalic anhydride (hereinafter, this compound is abbreviated to HHPA) and 1.0 part of benzyl-dimethylamine (hereinafter, this compound is abbreviated to BDMA), and the resulting mixture was thermally cured at 120°C for 4 hours and then at 150°C for 5 hours. A flexible cured material of the light yellowish, transparent resin (Cured material I) was obtained.

#### Example 2

100 parts of Nisso-PB-C-2000 ( $\bar{M}_n$ : 1964 and acid value: 37.1) were reacted with 100 parts of bisphenol-A diglycidyl-ether (epoxy equivalent: 190) at 135°C for 3.5 hours, and a resin (Resin II) having an acid value of 0.1 or less was obtained. Then, 100 parts of the Resin II were mixed with 34 parts of HHPA and 1.0 part of BDMA and the resulting mixture was treated by the same procedure as in Example 1. A resin cured material (Cured material II) was obtained.

#### Example 3

60 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1590 and acid value: 58.6) were mixed with 140 parts of bisphenol A diglycidyl ether (epoxy equivalent: 190) and 1.0 g of triethyl-amine, and the reaction of the resulting mixture was carried out at 145°C for two hours. A light yellowish, transparent resin (Resin III) having an acid value of 0.1 or less was obtained.

Then, 100 parts of the Resin III were mixed with 50 parts of HHPA and 1.0 part of BDMA, and the resulting mixture was thermally cured by the same procedure as in Example I. A cured resin material (Cured material III) was obtained.

#### Example 4

100 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1,560 and acid number: 60) were mixed with 100 parts of hydrogenated bisphenol A-diglycidyl ether (epoxy equivalent: 240), and a reaction of the resulting mixture was carried out at 150°C for 3.5 hours by blowing nitrogen gas in a reaction system. A colourless transparent resin (Resin IV) having an acid value of 0.1 or less was obtained.

Then, 100 parts of the Resin IV were mixed with 21 parts of HHPA and 1.0 part of BDMA and the resulting mixture was thermally cured by the same procedure as in Example I. A resin cured material (Cured material IV) was obtained.

#### 10 Example 5

100 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1,560, acid value: 59) were mixed with 200 parts of bisphenol-epichlorohydrin type epoxy resin (Epikote 1004, epoxy equivalent: 950) and 0.46 parts of tetrabutyl-ammonium-bromide (hereinafter, this compound is abbreviated to TBAB). A reaction of the resulting mixture was carried out in a kneader at 110°C for 7 hours by blowing nitrogen gas. After the reaction, the reaction product was cooled and ground. A white powdery resin (Resin V) having an acid value of 0.5 or less and a softening point of 90°C was obtained.

Then, 100 parts of the Resin V were mixed with 6 parts of tetrahydrophthalic anhydride (hereinafter, this compound is abbreviated to THPA) and 0.5 parts of TBAB. The resulting mixture was treated by compression moulding at 170°C for 1 hour, and a resin cured material (Cured material V) was obtained.

#### Example 6

100 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1,560, acid value: 59) were mixed with 230 parts of bisphenol-epichlorohydrin type epoxy resin (Epikote 1001, epoxy equivalent: 475) and 0.18 parts of TBAB. A reaction of the resulting mixture was carried out in a kneader at 100°C for 6 hours by blowing nitrogen gas. After the reaction, the reaction product was cooled and ground. A white powdery resin (Resin VI) having an acid value of 0.5 or less and a softening point of 40°C was obtained.

Thereafter, 100 parts of the Resin VI were mixed with 16.7 parts of THPA and 0.8 parts of TBAB. The resulting mixture was treated by compression moulding at 170°C for 1 hour, and a resin cured material (Cured material VI) was obtained.

#### Comparison Example 1

220 parts of Hycar CTBN 1300 × 8 (carboxyl terminated butadiene-acrylonitrile, copolymer,  $\bar{M}_n$ : 3,400 and acid value: 30.4) were reacted with 100 parts of bisphenol-A diglycidyl ether (epoxy equivalent: 190) at 145°C for 3.5 hours by blowing nitrogen gas in a reaction system. A light yellowish transparent resin (Resin I') having an acid value of 0.1 or less was obtained.

Then, 100 parts of the Resin I' were mixed with 19 parts of HHPA and 1.0 part of BDMA and the resulting mixture was thermally cured at 120°C for 4 hours and then at 150°C for 5 hours. A flexible cured material of light yellowish, transparent resin (Cured material I') was obtained.

Table 1 Properties of the Resins

Example Nos.	Resin Nos.	Appearance(1)	Viscosity(2) (Poise)	Acid Value	Life(3)
Example 1	I	light yellowish transparency	654	0.1 or less	6 months or more
Example 2	II	ditto	840	ditto	ditto
Example 3	III	ditto	13	ditto	ditto
example 4	IV	colorless transparency	225	ditto	ditto
Example 5	V	white powder	—	0.5 or less	ditto
Example 6	VI	white powder	—	ditto	ditto
Comparison Example 1	I'	light yellowish transparency	540	0.1 or less	ditto

(1) Appearance was judged by the naked eye

(2) Viscosity was measured with a Brookfield rotary viscometer at 40°C.

(3) 40°C was selected for a storage temperature and a terminal point was determined when its viscosity exceeded 10 times the initial viscosity.

Table 2 Properties of the cured material

Example Nos.	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparison Example 1
Cured material Nos.	I	II	III	IV	V	VI	I'
Dielectric constant	2.9	2.8	3.0	2.9	3.1	3.0	3.8
1MHZ (20°C)	2.8	2.7	2.8	2.7	2.9	2.8	3.6
Dielectric loss							
tangent	0.006	0.006	0.008	0.005	0.009	0.008	0.044
1MHZ (20°C)	0.006	0.006	0.007	0.005	0.009	0.008	0.020
Volume resistivity	10 <sup>18</sup> or more	10 <sup>18</sup> or more	10 <sup>18</sup> or more	10 <sup>18</sup> or more	10 <sup>18</sup> or more	10 <sup>16</sup> or more	10 <sup>14</sup> or less
Ω cm (20°C)	rupture does not occur	rupture does not occur	rupture does not occur	rupture does not occur	rupture does not occur	rupture does not occur	rupture does not occur
Bending strength kg/mm <sup>2</sup> (20°C)	32	55	8.6	50	65	62	21
Shore hardness D			77				
Temperature for heat distortion temperature (°C)	65.0	53.5	85.0	52.5	65	60	38
Cooling and heating re-cycling test	Crack does not occur	Crack does not occur	Crack does not occur	Crack does not occur	Crack does not occur	Crack does not occur	Crack does not occur
Note 1							



**Note 1: Cooling and heating re-cycling property test:**

The cooling and heating re-cycling test was carried out by placing the cured resin in a test tube and quickly cooling it at  $-50^{\circ}\text{C}$  for 30 minutes. It was then heated at  $150^{\circ}\text{C}$  and kept at the same temperature for one hour. These cooling and heating cycles were repeated for three times while watching for cracking.

**Examples 7 and 8**

The Resins I and II obtained in Examples I and II were each mixed with a diluent, filler, combustion-resistant agent, accelerator and stabilizer, as listed in Table 3, to provide Resin-compositions VII and VIII having good fluidity and workability as a casting material. The properties of the compositions are listed in Table III. The resin-compositions VII and VIII were thermally cured at  $120^{\circ}\text{C}$  for 4 hours. Resin cured materials (Cured materials VII and VIII) were obtained. The properties of the Cured material VII and VIII are listed in Table 3.

**Table 3**

			Example 7	Example 8	
20	compounding ratio	Resin I	85	—	20
		Resin II	—	70	
		allylglycidylether	15	—	
		styrene	—	30	
		powdery $\text{Al}(\text{OH})_3$	50	100	
		tetrabromobisphenol-A	20	20	
		tris(chloropropyl)	—	—	
		phosphate	10	—	
		antimony trioxide	10	10	
		methyltetrahydrophthalic anhydride	47	24	
30	BDMA	BDMA	1	0.5	30
		dicumylperoxide	—	0.5	
		cobalt-octonate	—	0.05 (calculated metal cobalt)	
35	3,5-di-tert-butyl-hydroxytoluene	0.05	0.05	0.05	35
40	properties of resin composition	appearance	[Resin-composition VII] white	[Resin-composition VIII] white	40
		viscosity (cps, $25^{\circ}\text{C}$ )	6500	6500	
		specific gravity ( $25^{\circ}\text{C}$ )	1.33	1.59	
		pot life (hours, $25^{\circ}\text{C}$ )	8	8	
45	properties of cured material	dielectric constant (20°C)	[Cured material VII] 3.3	[Cured material VIII] 3.4	45
		dielectric loss (20°C)	3.1	3.3	
		tangent (20°C)	0.009	0.006	
		volume resistivity $\Omega\text{-cm}$ (20°C)	0.009	0.006	
50	dielectric breakdown voltage KV/mm	dielectric breakdown voltage KV/mm	10 or more	10 or more	50
		Shore hardness D	23.0	24.2	
		bending strength Kg/mm (20°C)	68	79	
55	cooling and heating re-cycling test	cooling and heating re-cycling test	rupture does not occur	rupture does not occur	55
		crack does not occur	crack does not occur	crack does not occur	

*Comparison Example 2*

100 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1,560 and acid value: 60) were reacted with 35 parts of bis-phenol-A-diglycidyl ether (Epoxy equivalent: 190; Trade Name: Epikote 0828) at 200°C. The reactant mixture gelled for two hours or less after initiation of the reaction. A usable resin was not obtained.

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*Comparison Example 3*

100 parts of Nisso-PB-C-1000 ( $\bar{M}_n$ : 1,590 and acid value: 60) were reacted with 10 parts of 3,4-epoxy-cyclohexyl-methyl-3,4-epoxy cyclohexane-carboxylate (epoxy equivalent: 140) at 145°C. The reactant mixture gelled in the course of about one hour after initiation of the reaction. Again a usable resin was not obtained.

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**CLAIMS**

1. A method of producing a curable epoxy resin, comprising the step of reacting a carboxyl terminated polybutadiene or a carboxyl terminated butadiene-styrene copolymer with an epoxy resin selected from the group consisting of bisphenol-epichlorohydrin type epoxy resin and hydrogenated bisphenol-epichlorohydrin type epoxy resin in the ratio of 1.8 to 30 equivalent of the epoxy resin component per 1.0 equivalent of the carboxyl component at a temperature of 80 to 250°C for 1 to 20 hours.
2. A method of producing a curable epoxy resin, the method being substantially as hereinbefore described with reference to any one of Examples 1 to 8.
3. A curable epoxy resin when produced by the method as claimed in either claim 1 or claim 2.

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